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Conductivity as a Tool for Evaluating the Homogeneity of Sintered Discs of Transition Metal Oxides

by

R. Kershaw, B. Khazai, H. Leiva, K. Dwight and A. Wold

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CONDUCTIVITY AS A TOOL FOR EVALUATING THE HOMOGENEITY OF SINTERED DISCS OF TRANSITION METAL OXIDES

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ABSTRACT

Sintered discs can be prepared and made conducting for a number of transition metal oxides. It can be shown that room temperature resistivity measurements are an important tool in determining reproducibility for such materials. Several transition metal oxide systems have been chosen to illustrate the importance of these measurements.

Introduction

In the course of our studies (1) on the preparation and characterization of conducting n-type oxide electrodes, it was observed that the resistivities of well-sintered discs could be related to the purity and homogeneity of the products as well as to the reproducibility of the preparative procedures. It has been known, prior to these studies, that absolute resistivity measurements of sintered discs are extremely sensitive to variations in disc density, grain size, impurity concentration; however, there was little correlation between such measurements and the ability to reproduce sintered discs of known purity and homogeneity.

It will be shown that such correlations can be made and that for many systems preparative reproducibility can be measured for polycrystalline samples where single crystals are difficult to obtain. In this study, reproducibility of the absolute resistivities of well-sintered discs for several transition metal oxide systems will be compared to the

variation obtained with single crystal samples of the systems TiO_{2-x}, $TiO_{2-x}F_x$ and $SrTiO_{3-x}$.

Experimental

Single crystal samples of conducting TiO_{2-x}, $SrTiO_{3-x}$ and $TiO_{2-x}F_x$ were prepared from single crystal boules of TiO_2 and $SrTiO_3$ obtained from National Lead Industries. Reduced samples were prepared by heating wafers, 1 mm thick in a stream of pure hydrogen. Fluorination of TiO_2 wafers was carried out by the use of a Ar/H_2 carrier gas mixture containing hydrogen fluoride generated by the thermal decomposition of potassium bifluoride (2).

Bulk powder samples of $Sr_2Nb_2O_7$, $Ba_{.5}Sr_{.5}Nb_2O_6$, Ba_2FeNbO_6, Sr_2FeNbO_6, $FeNbO_4$ and other substituted iron niobates were prepared using standard solid-state techniques. The starting materials were carbonates and oxides of spectroscopic purity. Discs weighing between 150 and 200 mg were cold pressed at 60,000 to 90,000 P.S.I. In some cases, it was necessary to use a small amount of carbowax (Carbowax 20,000 Fisher Scientific Co.) as a binder. These discs were generally sintered by placing them on a bed of powder having the same composition. This was contained in a covered alumina crucible, which was then slowly heated up to and held at the desired sintering temperature as given in Table I.

TABLE 1

Sample Preparation and Reducing Conditions of Discs

Composition	Preparation Conditions		Reducing Conditions		
	Temp., °C	Time, hr.	Red. Agent	Temp.	Time
$Sr_2Nb_2O_7$	1330	15	Nb	900	67
$Ba_{.5}Sr_{.5}Nb_2O_6$	1330	15	Nb	900	67
Sr_2FeNbO_6	1330	6	Fe	950	72
$FeNbO_4$	1250	24	none	Discs sintered in	
$Fe_{.9}Cr_{.1}NbO_4$	1250	24	none	air at 1250°C for	
$Fe_{.9}In_{.1}NbO_4$	1250	24	none	24 hours.	
$Fe_{.9}V_{.1}NbO_4$	900	24	none	Discs sintered in evacuated silica tube at 900°C for 24 hours.	

A disc was considered well sintered when its measured density was greater than 95% of the theoretical density. Sample densities were determined using a hydrostatic technique (3) employing a Mettler Model H54 analytical balance.

The density medium perfluoro (1-methyldecalin) was chosen because of its relatively low vapor pressure and its ability to wet the samples. A high purity silicon crystal ($\rho = 2.328 g/cm^3$) was chosen for calibrating the density liquid. In order to obtain reproducible results, care was taken to outgas the samples thoroughly prior to density measurements.

Conductivity for $FeNbO_4$ was achieved by sintering the discs at 1250° for 24 hours in a hollow globar furnace and allowing the sample to cool at a rate of 75°/hour. Reduction of $Sr_2Nb_2O_7$, $Ba_{.5}Sr_{.5}Nb_2O_6$, Ba_2FeNbO_6 and Sr_2FeNbO_6 was achieved by heating the discs in sealed evacuated silica tubes containing either niobium or iron (4). As described by Schleich (5), the niobium or iron powder was placed in a small silica tube so that the sample and reducing material were not in direct contact. The conditions for the various reductions are given in Table 1.

Results and Discussion

X-ray diffraction patterns were obtained from ground portions of the final discs using the Debye-Scherrer method. These patterns were compared with those obtained from the polycrystalline reaction products.

Electrical measurements of the single crystal samples $SrTiO_3$, TiO_2 and $TiO_{2-x}F_x$ were made on bars 4 x 2 x 1 mm cut from the reduced or fluorinated wafer. Each bar was further subdivided into three sections 4 x 2 x 0.25 mm in order to establish whether or not each wafer was truly homogeneous. Thus, the middle section was taken entirely from the interior of the wafer and made no contact with the outside surface. Indium leads were bonded ultrasonically to each section, and the standard Van der Pauw technique (6) was used to measure its resistivity. Excellent agreement between the resistivity values for inside and outside sections was obtained for the reduced or fluorinated wafers and these results are given in Table 2.

TABLE 2

Reproducibility of Resistivity Measurements for Single Crystal Wafers of TiO_2, $TiO_{2-x}F_x$ and $SrTiO_{3-x}$

Sample Composition	Resistivity of Inside Section	Resistivity of Outside (I)	Resistivity of Outside (II)
	(Ω-cm)	(Ω-cm)	(Ω-cm)
$TiO_{1.999}$	6.0	6.4	6.3
$TiO_{1.993}$	0.9	0.9	1.0
$TiO_{1.9998}F_{.0002}$*	5.4	5.7	5.2
$SrTiO_{3-x}$** I	0.14	0.15	0.16
II	0.053	0.052	0.051

* limit of fluorine analysis

**values of x were not determined

For sintered discs of the polycrystalline samples, the measured resistivities were generally observed to decrease with increasing time of reduction; however, the rate of reduction became small after 72 hours. As can be seen from Table 3, resistivities were measured before and after abrasion of the discs by sandblasting to two-thirds of their original thickness.

TABLE 3

Resistivity of Sintered Discs Before and After Sanding

Sample	ρ Before Sanding	ρ After Sanding
	Ω-cm	Ω-cm
$Sr_2Nb_2O_7$ I	41.5	40.9
II	209	210.5
$Ba_{.5}Sr_{.5}Nb_2O_6$ I	2.58	2.67
II	2.35	2.50
Sr_2FeNbO_6	112	110
$FeNbO_4$	40	39.3
$Fe_{.9}Cr_{.1}NbO_4$	52	52.3
$Fe_{.9}In_{.1}NbO_4$	67.4	68.1
$Fe_{.9}V_{.1}NbO_4$	83.6	84.1

A negligible observed change in the measured resistivity after such abrasion established the homogeneity of the products.

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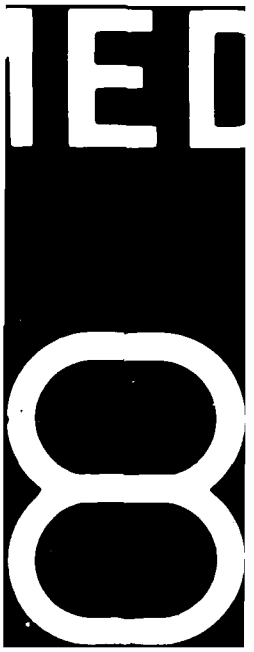
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